Short communication

Adsorption of phenolic compounds from aqueous solution onto a macroporous polymer and its aminated derivative: isotherm analysis

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Abstract

Adsorption of phenolic compounds from aqueous solution to a macroporous polymeric adsorbent (CHA-111), its animated derivative (MCH-111) and a reference weakly anion exchanger (ND-900) was studied. Experimental results indicated that amino functional groups on the polymeric matrix play an important role in phenol adsorption by MCH-111 and ND-900, which was attributed to the formation of hydrogen bonding between the phenol molecule and the amino group on the polymeric matrix. The semi-empirical Freundlich isotherm equation and its reduced form were employed to interpret the adsorption behavior. A site energy distribution model based on the Polanyi adsorption potential theory can elucidate the adsorption mechanism reasonably.
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Keywords: Phenolic compounds; Adsorption isotherm; Polymeric adsorbent; Amination; Site energy distribution

1. Introduction

Phenolic compounds are commonly encountered organic contaminants in environmental systems [1]. Effective treatment of industrial wastewater containing these chemicals should be required before discharge into the receiving water body [2–7]. Adsorption of phenolic compounds on activated carbon and various oxidation processes have been considered as a potential treatment technique [8], and adsorption of phenols and other weak electrolytes on activated carbon has been discussed elsewhere [9–12]. In recent years, polymeric adsorbents have been increasingly regarded as an alternative to activated carbon due to their feasible adsorption–regeneration properties and perfect mechanical intensity. A macroporous hypercrosslinked polymer CHA-111 was reported to be ideal for removing phenols and other compounds from aqueous solution [13,14]. Since the invention of the hyper-crosslinked polymeric adsorbent by Danvakov and Tsyurupa [15,16], it has achieved wide applications in many fields such as separation and analysis because of its unique adsorption properties including ideal pore structure and various surface functional groups available. These functional groups introduced to the polymer matrix are able to modify the surface chemistry of the adsorbent allowing specific adsorbent–adsorbate interactions and then to improve adsorption behavior of organic compounds [7,17]. Specifically, research has focused on surface chemical modification by introducing acetyl and *o*-carboxybenzoyl groups [18], benzoyl and hydroxymethyl functionalities [19] onto the polymeric matrix.

The current study was aimed at chemical modification of CHA-111 by amination reaction to improve the adsorption behavior for phenolic compounds. Adsorption isotherms were analyzed using the semi-empirical Freundlich model and its reduced form. A site energy distribution model based on the Polanyi adsorption potential theory was employed to describe the adsorption behavior on polymeric adsorbents.

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Table 1
Some physical and chemical characteristics of phenolic compounds

Substance	Phenol	p-Cresol	p-Nitrophenol	p-Chlorophenol	2,4-Dinitrophenol	2,4-Dichlorophenol
pK_a (298 K)[a]	9.89	10.17	7.15	9.18	3.96	7.85
Solubility (%)[b]	7.65	1.92	1.05	2.53	0.033	0.54
Adsorbate-covered area ($\times 10^5$ m^2/mol)[c]	3.00	–	4.26	3.63	5.15	4.21
λ_{max} (nm)	270	276	223	280	262	285

[a] Taken from reference [21].
[b] Measured at 298 K.
[c] Obtained from reference [22].

2. Experimental

2.1. Adsorbents

A macroporous hypercrosslinked polymeric adsorbent CHA-111 and a weakly basic exchanger ND-900 were obtained from Langfang Electrical Resin Co. Ltd., Hebei Province, China. The amination process of adsorbent CHA-111 is described elsewhere [20], and the aminated derivative was labeled as MCH-111. All the adsorbents were extracted by ethanol for 8 h in a Soxlet apparatus and then dried under vacuum at 325 K for 3 h before use. Surface area and pore-size distribution of the adsorbents were analyzed with a Micromertics 2010C automatic analyzer (USA).

2.2. Adsorbates

All the phenolic compounds tested in this study were purchased from Shanghai Chemical Reagent Station (Shanghai, China) and used without further purification. Their physical and chemical characteristics are listed in Table 1.

2.3. Adsorption isotherms

Batch adsorption tests were carried out using the bottle-pointed method as follows: 0.25 g of each adsorbent was first added to a 250-mL flask containing 100 mL of aqueous phenol solution of known concentration. The flask was then transferred to a G 25 model incubator shaker (New Brunswick Scientific Co., USA) preset at desired temperature. The sample was shaken at 200 rpm for 24 h to ensure adsorption equilibrium. The concentrations of phenols in equilibrium (C_e) were determined. The initial concentrations (C_0) of the solutions range from 200 to 1400 mg/L depending on their solubility in water. The adsorbent-phase concentrations of adsorbates Q_e (mg/g) were calculated by conducting a mass balance on phenol using the following equation:

$$Q_e = \frac{V_1(C_0 - C_e)}{W} \tag{1}$$

where V_1 is the volume of solution and W is the mass of dry resin.

The concentrations of adsorbates were analyzed spectrometrically with a Helious Betra UV–vis spectrometer (Unicam Co., UK) at different wavelengths as required.

2.4. Isotherm modeling

The semi-empirical Freundlich equation was employed to describe the adsorption data for phenolic compounds [8]:

$$Q_e = K_F C_e^n \tag{2}$$

where K_F is the Freundlich parameter for a heterogeneous adsorbent; n is related to the magnitude of the adsorption driving force and the site energy distribution of the adsorbent.

Generally n represents the heterogeneity of site energy distribution in the adsorbents while K_F is generally interpreted as a "capacity" parameter [23]. The above isotherm parameters can be determined graphically by plotting $\ln Q_e$ against $\ln C_e$ according to Eq. (2).

3. Results and discussion

3.1. Characterization of the polymeric adsorbents

Characterization of the three polymeric adsorbents used in this study is presented in Table 2. The average size of the aminated polymeric particle was found identical to the original one. However, the BET surface area slightly decreased from 721.5 to 671.5 m^2/g adsorbent. The loss of macropore volume (from 0.36 to 0.16 cm^3/g) indicates that amination occurs mainly in the macroporous region. The highest content of amino groups exists on ND-900 among these adsorbents, while its BET surface area and micropore volume are the lowest.

Table 2
Characteristics of the polymeric adsorbents

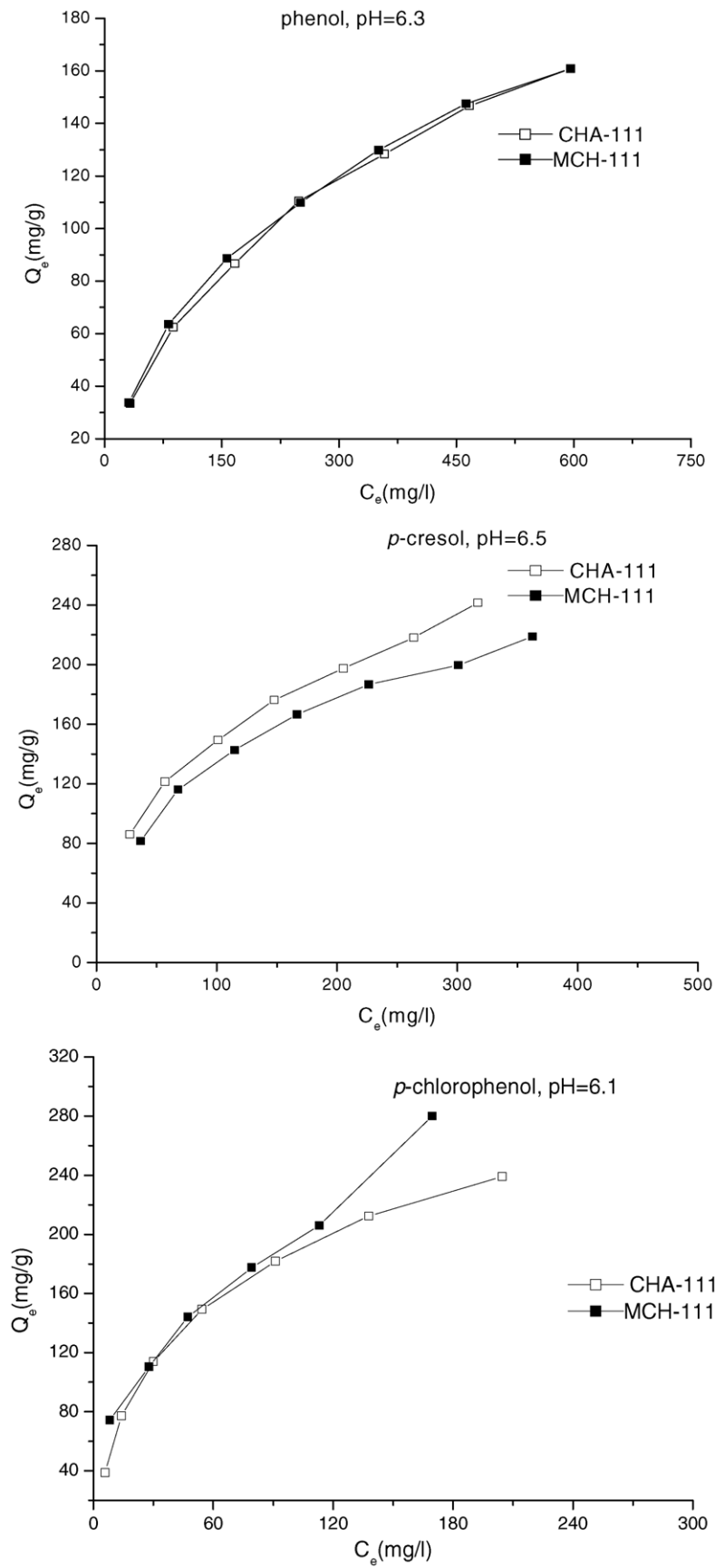| Polymeric adsorbent	CHA-111	MCH-111	ND-900
Structure	Polystyrene	Polystyrene	Polystyrene
BET surface area (m^2/g)	721.5	671.5	31.8
Crosslinking density (%)[a]	>40	>40	~8
Macropore volume (cm^3/g)	0.36	0.16	0.28
Mesopore volume (cm^3/g)	0.028	0.028	0.0002
Micropore volume (cm^3/g)	0.42	0.40	0.0028
Average pore diameter (nm)	1–2	1–2	8–10
Tertiary amino group (mmol/g)	0	1.534	3.781

[a] Provided from the manufacturer.

Fig. 1. Adsorption isotherms of phenolic compounds on CHA-111 and MCH-111.
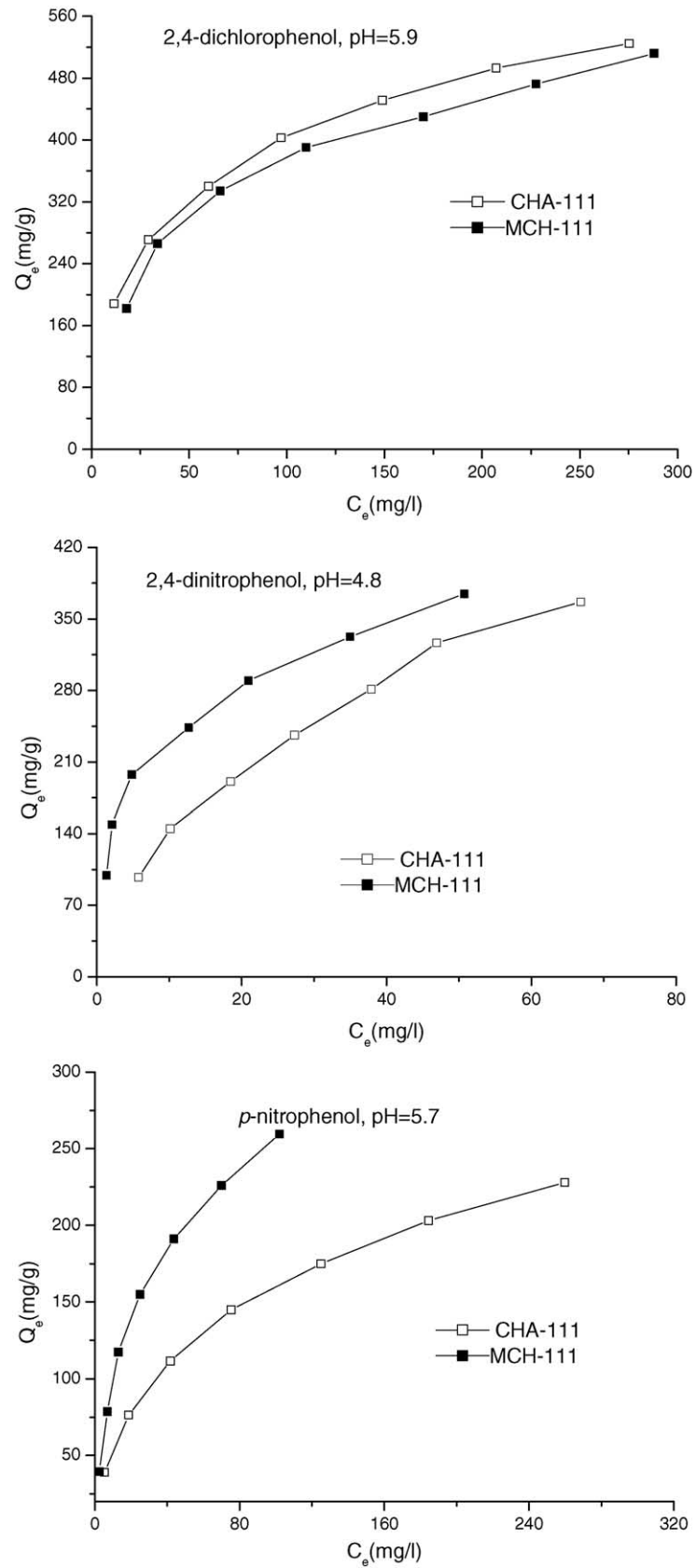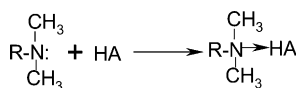
Fig. 1. (*Continued*).

Table 3
Freundlich isotherm parameters for phenol adsorption on the polymeric adsorbents

Adsorbate	Adsorbent	$\ln K_F$	n	R^2
Phenol	CHA-111	1.67	0.541	0.995
	MCH-111	1.97	0.494	0.998
	ND-900	0.265	0.659	0.998
p-Cresol	CHA-111	3.14	0.413	0.998
	MCH-111	3.20	0.372	0.996
	ND-900	−0.833	0.765	0.999
p-Chlorophenol	CHA-111	3.28	0.422	0.992
	MCH-111	3.51	0.389	0.993
	ND-900	2.11	0.565	0.999
p-Nitrophenol	CHA-111	2.95	0.457	0.993
	MCH-111	3.60	0.431	0.986
	ND-900	3.52	0.402	0.999
2,4-Dichlorophenol	CHA-111	4.49	0.323	0.994
	MCH-111	4.58	0.292	0.970
	ND-900	2.46	0.543	0.999
2,4-Dinitrophenol	CHA-111	3.55	0.554	0.997
	MCH-111	4.78	0.268	0.999
	ND-900	4.97	2.44	0.994

3.2. Freundlich adsorption isotherms

Graphic presentations of the adsorption isotherms are illustrated in Fig. 1, and the isotherm parameters based on Eq. (1) are listed in Table 3. As shown in Table 3, for the adsorption of all the adsorbates on MCH-111, K_F increases as n decreases. The increase in K_F of the aminated adsorbent corresponds to more active sites while the decrease in n may be regarded as increased surface heterogeneity after animation. For adsorption of phenolic compounds on MCH-111, the acid–base interaction should be taken into account by the following schematic representation and the phenolic molecules would be bounded on the polymeric surface by such interaction [20,24–26]:

$$\begin{array}{c} CH_3 \\ | \\ R\text{-}N: \\ | \\ CH_3 \end{array} + HA \longrightarrow \begin{array}{c} CH_3 \\ | \\ R\text{-}N \text{→} HA \\ | \\ CH_3 \end{array}$$

where R is the polymeric backbone; and HA is the phenolic adsorbate.

According to the different adsorption capacity on CHA-111 and MCH-111 (shown in Fig. 1), the positive effect of amino group can be observed on adsorption capacity of phenolic compounds with lower pK_a values, such as *p*-nitrophenol and 2,4-dinitrophenol, while a negligible or even negative effect occurs for pheolic compounds with higher pK_a values, such as phenol and cresol. When adsorption from aqueous solution on MCH-111 is considered, water molecules can also occupy the amino group by hydrogen-bonding interaction and form water clusters near the functional groups. Effective adsorption of phenolic molecules on the amination sites occurs only after expelling the water cluster occupied before. Those with lower pK_a values present stronger acid–base interaction to expel the occupied water cluster for their higher polarity, and a positive effect will be observed on them. Lower adsorption capacity for *p*-cresol on MCH-111 than CHA-111 may be attributed to its negligible hydrogen-bonding interaction and the loss of pore volume after amination of CHA-111 (as listed in Table 2).

For phenol adsorption on ND-900, hydrogen-bonding interaction is assumed to play a dominant role because of its negligible micropore volume as compared with CHA-111 and MCH-111. As shown in Fig. 2, Q_e of 2,4-dinitrophenol on ND-900 is the largest while that of *p*-cresol is the smallest among all the tested compounds. This difference is consistent
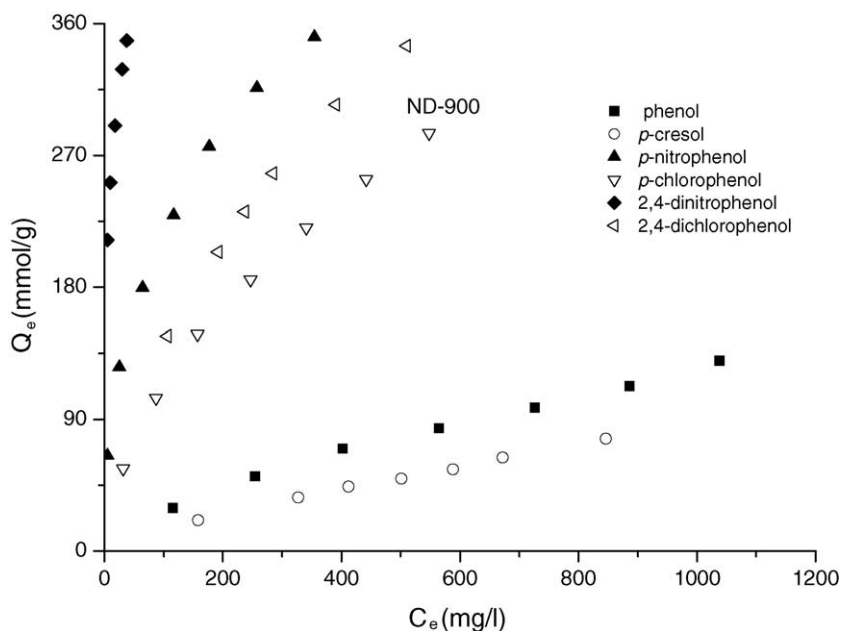

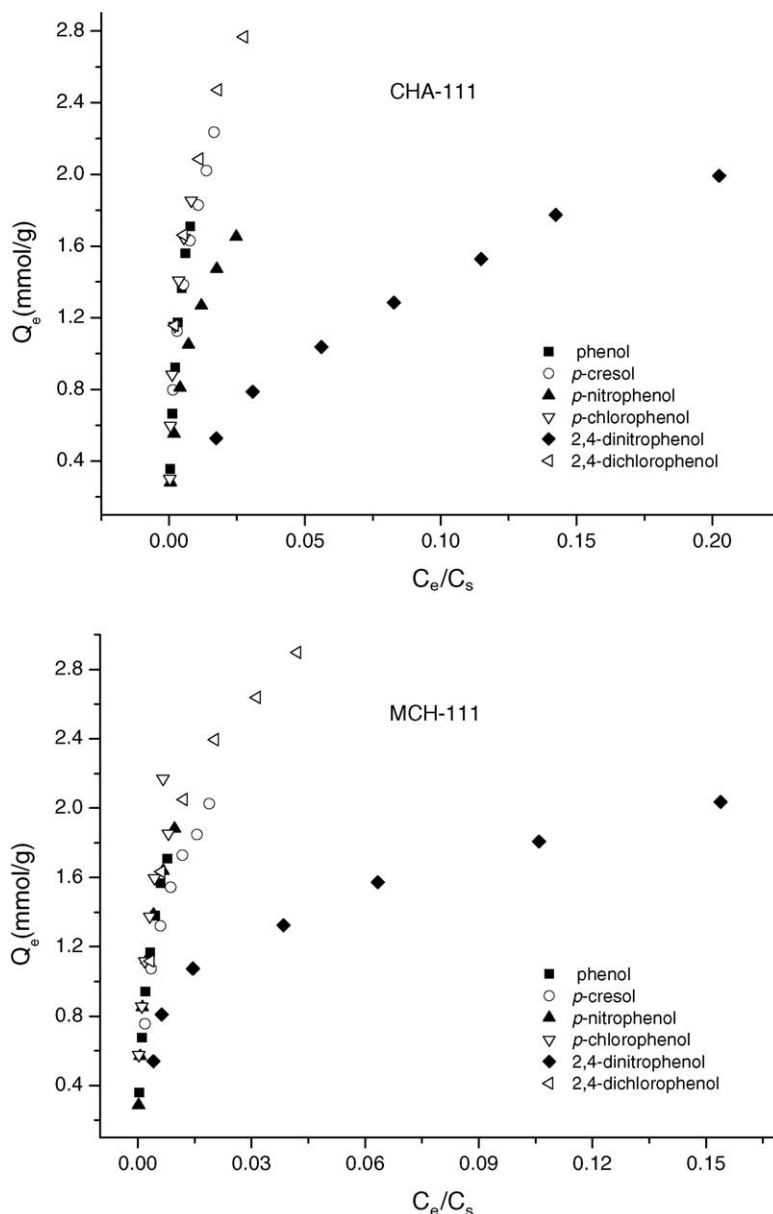Fig. 2. Adsorption isotherms of phenolic compounds on ND-900.

Fig. 3. Reduced Freundlich isotherms of phenol adsorption on CHA-111 and MCH-111.

with the order of pK_a values and the strongest affinity occurs between 2,4-dinitrophenol and ND-900 while the weakest affinity occurs for *p*-cresol.

3.3. Modified Freundlich adsorption isotherm

In general, adsorption involves the accumulation of molecules from a solvent onto the exterior and interior (i.e. pores) surfaces of an adsorbent. This surface phenomenon is a manifestation of complicated interactions among the three components involved, i.e. the adsorbent, the adsorbate and the solvent. Normally, the affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption. However, the adsorbate–solvent affinity can also play a significant role in adsorption. In order to account for such

affinity, the normalized adsorbate concentration (C_e/C_s) is used to describe the modified Freundlich equation as [22,27]:

$$Q_e = K_F' \left(\frac{C_e}{C_s} \right)^n \tag{4}$$

The isotherm data were replotted using Q_e (mmol/g) versus the normalized aqueous concentration and are presented in Fig. 3. Fig. 3 shows that almost all the adsorption isotherms of phenolic compounds on CHA-111 and MCH-111 overlap except for part of *p*-nitrophenol and 2,4-dinitrophenol. This observation is similar to that reported by Urano et al. that the adsorption isotherms for substituted benzoic acids from aqueous solution on GAC were approximately overlapped on each other [27].
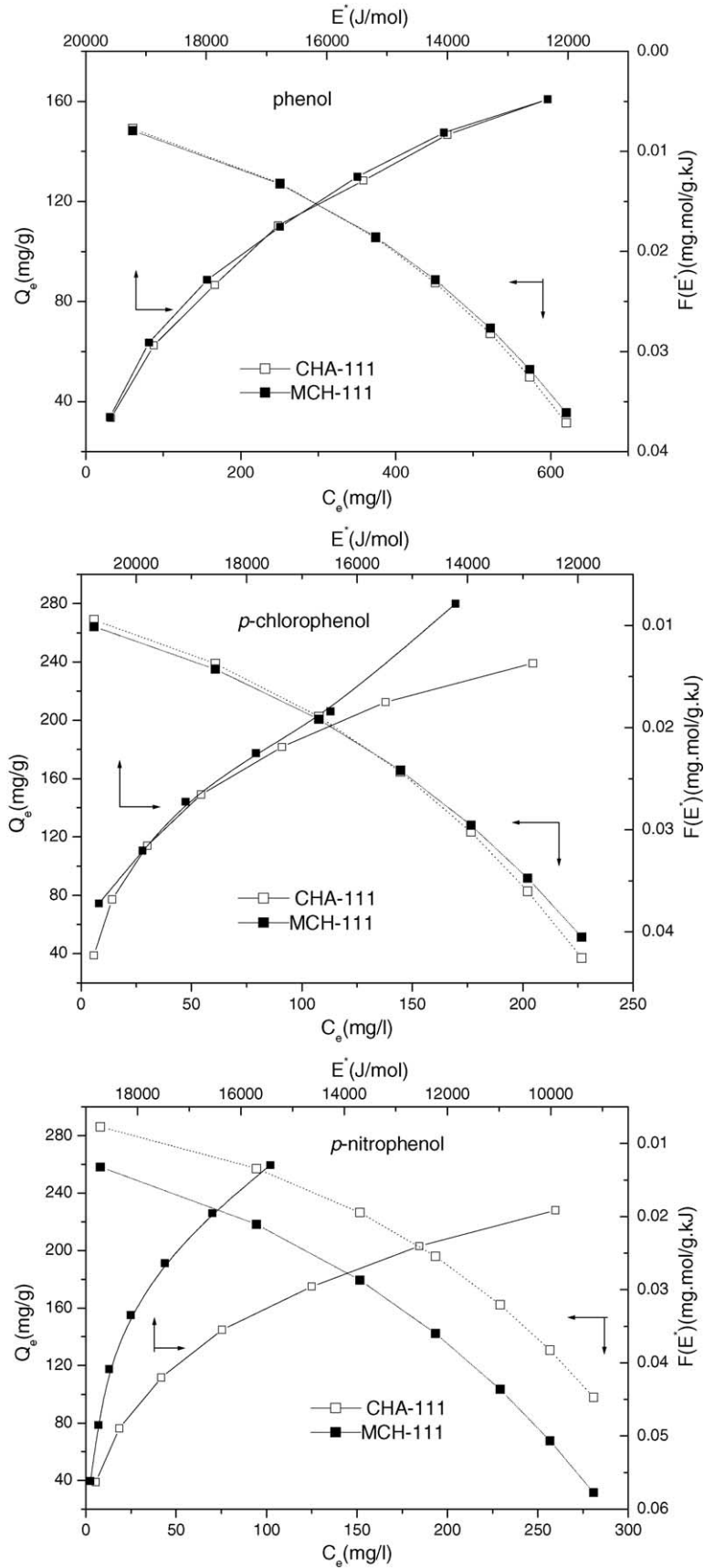
Fig. 4. Site adsorption energy distribution of phenolic compounds on the polymeric adsorbents.

Table 4
Dipole moment data of some substituted benzenes in gas phase [28]

Compounds	Dipole moment (D)
C_6H_6	0
$C_6H_5CH_3$	0.37
C_6H_5Cl	1.75
m-$C_6H_4Cl_2$	1.68
$C_6H_5NO_2$	4.28
m-$C_6H_4(NO_2)_2$	4.25

Generally, π–π interactions between aromatic rings of adsorbates and polymeric matrix play an important role in adsorption of phenolic compounds on CHA-111. The electron density of aromatic ring should be taken into account for its effect on π–π interactions. It is well known that the substituted groups can either strengthen or weaken the electron cloud distribution on aromatic rings in accordance with their different dipolar properties. Table 4 lists the dipole moment data of several substituted benzenes in the gas phase. Both nitro and 2,4-dinitro groups will be expected to have stronger effects on π–π interactions due to their high dipole moment, as compared with methyl, chloro and 2,4-dichloro groups. Thus, the isotherms of p-nitrophenol and 2,4-dinitrophenol deviate substantially from others. The size exclusion (steric) effect should also be taken into account in the deviation. Larger molecular sizes of nitrophenols cause them to occupy more area on the adsorbent surface, which results in the lower adsorption capacity [22]. For p-nitrophenol adsorption on MCH-111, such deviation becomes negligible due to the positive effect on capacity by the hydrogen bonding interaction.

3.4. Effect of amination on site energy distribution

The basic integral equation underlying the theory of heterogeneous surface [29] is:

$$Q_e(C_e) = \int_0^\infty Q_h(E, C_e)F(E)dE \qquad (5)$$

This equation defines the total adsorption (Q_e) of a solute by a heterogeneous surface as the integral of an energetically homogeneous isotherm (Q_h) multiplied by a site energy frequency distribution ($F(E)$) over a range of energies, where E is the difference between the solute and solvent adsorption energies for a given site. According to the Polanyi adsorption potential theory [30], the equilibrium liquid-phase concentration is related to the energy of adsorption by:

$$C_e = C_s \exp -\left(\frac{E - E_s}{RT}\right) = C_s \exp\left(\frac{-E^*}{RT}\right) \qquad (6)$$

where C_s is the maximum solubility of the solute in the solvent, E_s the adsorption energy corresponding to $C_e = C_s$, R the universal gas constant, T the absolute temperature and $E^* = E - E_s$.

By incorporation Eq. (6) into Eq. (5), an approximate site energy distribution, $F(E^*)$, is obtained by differentiating this isotherm, $Q(E^*)$, with respect to E^* as follows:

$$F(E^*) = \frac{-dQ(E^*)}{dE^*} \qquad (7)$$

Incorporation of Eq. (6) into the Freundlich equation followed by differentiation with respect to E^* (Eq. (7)) yields:

$$F(E^*) = \frac{K_F n C_s^n}{RT} \exp\left(\frac{-nE^*}{RT}\right) \qquad (8)$$

Fig. 4 illustrates the correlation between $F(E^*)$ and E^* of phenol adsorption on two adsorbents including the adsorption isotherms for comparison. The isotherms are in good agreement with the $F(E^*)$–E^* curves. For example, adsorption isotherms of phenol on both adsorbents overlaps and the $F(E^*)$–E^* curves for phenol adsorption overlaps simultaneously, while adsorption capacity of p-nitrophenol on MCH-111 is greater than CHA-111 and the similar results can also be obtained from the $F(E^*)$–E^* curves. Therefore, the Polanyi adsorption potential theory can reasonably describe phenol adsorption on CHA-111 and MCH-111.

4. Conclusions

Chemical modification of a macroporous adsorbent CHA-111 with dimethylamine was carried out to obtain an aminated derivative MCH-111. For phenolic compounds with lower pK_a values, higher adsorption capacities on MCH-111 than CHA-111 were observed due to hydrogen bonding interactions between the amino groups and adsorbate molecules. The semi-empirical Freundlich equation and its reduced form allowed for interpretation of the adsorbent–adsorbate interaction. A site energy distribution model based on the Polanyi adsorption potential theory is consistent with the isotherm data for both adsorbents and can reasonably elucidate the adsorption mechanism.

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